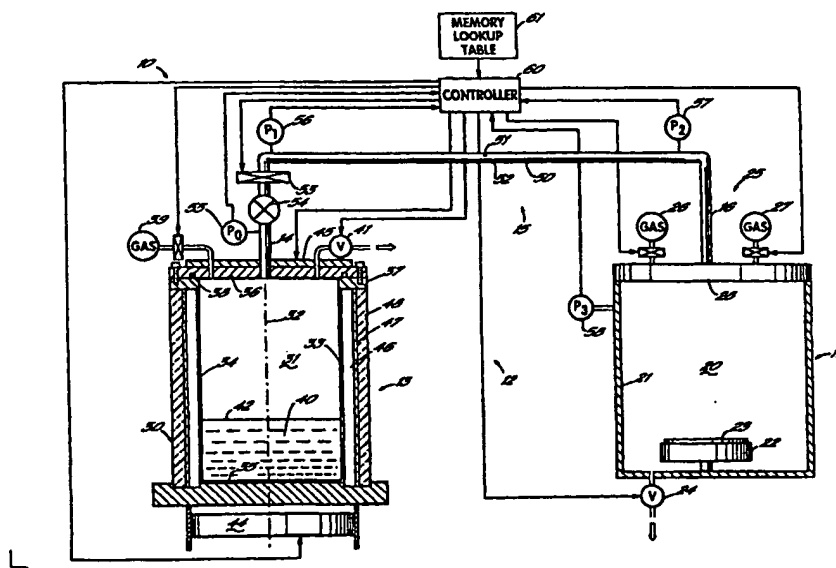


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(54) Title: CVD TiN PLUG FORMATION FROM TITANIUM HALIDE PRECURSORS



## (57) Abstract

A method of depositing high quality titanium nitride (TiN) films and filling small contacts having high aspect ratio features using TiN. The method uses a CVD process with titanium tetraiodide (TiI<sub>4</sub>) as a precursor material. The method allows TiN films with a thickness greater than about 0.3  $\mu\text{m}$  to be deposited without cracking. For sufficiently high TiN deposition rates and sufficiently low TiN resistivities the preferred process temperature is at least about 500 °C. The method varies process pressure to obtain a seamless TiN plug fill in high aspect ratio structures.

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**CVD TiN PLUG FORMATION FROM TITANIUM HALIDE PRECURSORS****Field of the Invention**

This invention relates to the formation of integrated circuits, and specifically to chemical vapor deposition of titanium nitride films from titanium halide precursors.

**5   Background of the Invention**

Integrated circuits provide the pathways for signal transport in an electrical device. An integrated circuit (IC) in a device is composed of a number of active transistors contained in a silicon base layer of a semiconductor substrate. To increase the capacity of an IC, large numbers  
10 of interconnections with metal "wires" are made between one active transistor in the silicon base of the substrate and another active transistor in the silicon base of the substrate. The interconnections, collectively known as the metal interconnection of a circuit, are made through features such as holes, vias or trenches that are cut into a substrate. The particular  
15 point of the metal interconnection which actually makes contact with the silicon base is known as the contact. The remainder of the hole, via or trench is filled with a conductive material, termed a contact plug. As

transistor densities continue to increase, forming higher level IC, the diameter of the contact plug must decrease to allow for the increased number of interconnects, multilevel metalization structures and higher aspect ratio vias.

5                    Vias greater than about  $0.16\text{ }\mu\text{m}$  in diameter are typically filled as follows. A liner of about  $100\text{ }\text{\AA}$  titanium (Ti) is first deposited using either CVD or PVD. This Ti layer enhances the electrical contact to the silicon base layer. A liner of about  $500\text{ }\text{\AA}$  titanium nitride (TiN) is then deposited on the Ti layer. Deposition may be by either CVD or PVD, with  
10    low pressure CVD (LPCVD) preferred because only LPCVD provides the conformality, defined as the ability to exactly reproduce the surface topography of the underlying substrate, necessary to cover the bottom and sidewalls of submicron structures with high aspect ratios. The TiN layer serves as a metal diffusion barrier to protect Ti from corrosive attack by  
15    fluorine (F) during subsequent tungsten (W) deposition from  $\text{WF}_6$ . TiN also serves as an adhesion layer for W since W does not adhere to metal oxides. While TiN provides an excellent contact barrier, the TiN must have a thickness of about  $500\text{ }\text{\AA}$  to be effective as a barrier. If the TiN thickness is less than about  $500\text{ }\text{\AA}$ , Ti metal diffuses into the silicon. The remainder  
20    of the plug is then filled with W deposited by CVD. W is used because of its low electrical resistivity and its reliability in forming contact plugs. The W layer provides an area of low resistance, which is important for current conduction in an IC. The surface of the contact plug is then etched or

polished. The resulting planarized surface is necessary for optimal metal interconnections, and thus for optimal function of the IC.

As transistor densities continue to increase, features continue to be small, that is, having a diameter of  $0.25\ \mu\text{m}$  or less. The diameter of the contact plug must decrease to allow for the increased number of interconnections. For vias with a diameter of less than about  $0.16\ \mu\text{m}$ , however, the resistance of the contact plug metalization layer is dominated by the TiN diffusion barrier layer. Since the TiN barrier layer must remain at about  $500\ \text{\AA}$  for robust performance as a diffusion barrier, it follows that the portion of the contact plug that is filled with W is diminished. For example, a structure with a diameter of  $0.15\ \mu\text{m}$  would have a W film or "core" in the center of the plug that is only about  $300\ \text{\AA}$ . Therefore, the effective plug resistance becomes dominated more by the higher resistivity TiN and, more importantly, the resistance of the interface between the TiN and W layers.

Subsequent filling of the contact plugs with W, then, provides an extra procedural step with no significant effect on the overall resistance of the contact plug. Accordingly, a process step in the formation of an IC could be eliminated, and manufacturing efficiency could be increased by filling a via with a contact plug of TiN only, rather than with TiN and W. Therefore, what is needed is a method of forming a TiN contact plug by CVD and eliminating a W layer in the contact plug in the formation of an IC.

TiN films deposited by CVD, however, have relatively high stress. A film with high stress has a high intensity of internally distributed forces or components of forces that resist a change in volume or shape of the film when the film is subjected to external forces. The high stress limits the maximum film thickness that can be deposited. Typically, the maximum thickness of a TiN film deposited by CVD over conventional first level oxides is about 800 Å. TiN films that are thicker than about 800 Å begin to crack due to internal stress in the film. Microcracks, appearing at the TiN film surface and defined as discontinuities in the surface material that are large enough to increase resistance of the film, thus result in suboptimal performance of an IC.

While the absolute thickness of the W layer may vary according to the size of the via to be filled, its relative thickness is about 80% of the via diameter. This is because the deposited film must not only fill the volume of the via with a contact plug, but it must also fill the "dimple" above the contact plug. The "dimple," defined as an indentation in the TiN that is formed during filling of the via, is eliminated by depositing more TiN on top of the plug, resulting in a capping layer. Thus, for a 0.25  $\mu\text{m}$  feature, a TiN film having a thickness of 2000 Å ( $0.8 \times 2500$  Å) is required. For a good plug fill it is also critical that the film be continuous, completely conformal, and seamless. A conformal film is one that exactly reproduces the surface topography of the underlying substrate. A seamless film is one that contains no cracks.

A CVD method of filling a via in a substrate with a TiN plug and capping with a TiN layer has been disclosed in U.S. Patent Application Serial No. 08/964,532 assigned to Tokyo Electron Limited and incorporated by reference herein in its entirety. These features are not available with existing TiN depositions by CVD processes using  $\text{TiCl}_4$  precursors. With  $\text{TiCl}_4$  precursors, the films consistently crack when thicknesses exceed about 500-800 Å. Cracking is unacceptable because it prevents adhesion of the film to the underlying layers, resulting in the film "flaking off" and thus compromising subsequent processes. Cracking also increases the expected electrical resistivity of the plug.

Therefore, a method of filling a high aspect ratio via with a high quality conformal contact plug of TiN without cracking is desired. Such a film would eliminate a W deposition step, and thus reduce the number of process steps to fill the contact. This would represent a significant savings for device fabrication.

#### Summary of the Invention

To this end, and in accordance with the principles of the present invention, a method of filling a high aspect ratio via with a TiN plug and eliminating a tungsten (W) deposition step is disclosed. The TiN plug is deposited by CVD from a titanium iodide (TiI) precursor. The preferred TiI precursor is titanium tetraiodide ( $\text{TiI}_4$ ) and is deposited by thermal CVD.

The present invention is also directed to a method of completely filling a high aspect ratio via which is less than about  $0.16\ \mu\text{m}$  in diameter with a TiN layer deposited by CVD.

The invention is also directed to a method of forming a contact  
5 plug in a via of an IC by CVD of a TiN layer provided by a  $\text{TiI}_4$  precursor. The via is a high aspect ratio via that is less than about  $0.16\ \mu\text{m}$  in diameter.

The TiN film that fills the contact plug according to the invention is 100% conformal with the underlying topography. Films that  
10 are 100% conformal are beneficial because they exactly reproduce the surface topography of the underlying substrate, which allows optimal function of an IC. Thus, this method is useful to completely fill high aspect ratio features. Another advantage of the method is the elimination of a separate process step in which W is deposited, saving both time and  
15 expense. The method also eliminates the problem of adhering a W layer to TiN. These and other objects and advantages of the present invention will be made apparent from the accompanying drawings and description thereof.

#### **Brief Description of the Drawings**

FIG. 1 is a schematic of an apparatus for chemical vapor  
20 deposition (CVD).

FIG. 2 is a graph comparing stress in titanium (TiX) halide based titanium nitride (TiN) films.



FIG. 3 is a photograph of a SEM of a titanium tetraiodide ( $TiI_4$ ) based TiN film.

FIGS. 4A and 4B are transmission electron micrographs of Ti halide based TiN films.

5           FIG. 5 is a photograph of a SEM of a 10:1 aspect ratio structure filled with TiN deposited by CVD at a pressure of 1.5 Torr.

FIG. 6 is a photograph of a SEM of a 10:1 aspect ratio structure filled with TiN deposited by CVD at a pressure of 1.0 Torr.

10           FIG. 7 is a photograph of a SEM of a 10:1 aspect ratio structure filled with TiN deposited by CVD at a pressure of 1.0 Torr.

#### **Detailed Description**

In chemical vapor deposition (CVD) processes, gas precursors are activated using either thermal energy or electrical energy. Upon activation, the gas precursors react chemically to form a film. A preferred method of CVD is illustrated in FIG 1 and is disclosed in a copending application entitled APPARATUS AND METHOD FOR DELIVERY OF VAPOR FROM SOLID SOURCES TO A CVD CHAMBER by Westendorp et al., assigned to Tokyo Electron Limited, filed on the same date as the present application and incorporated by reference in its entirety. A chemical vapor deposition (CVD) system 10 includes a CVD reaction chamber 11 and a precursor delivery system 12. In the reaction chamber 11, a reaction is carried out to convert a precursor gas of a titanium halide compound, for example, titanium iodide ( $TiI_3$ ) into a film such as a barrier layer film of TiN.

The precursor delivery system 12 includes a source 13 of precursor gas having a gas outlet 14, which communicates through a metering system 15 with a gas inlet 16 to the CVD reaction chamber 11. The source 13 generates a precursor gas, for example a Til vapor from the  
5    respective Til compound, preferably  $TiI_4$ . The compound is one that is in a solid state at standard temperature and pressure. The precursor source is maintained, preferably by controlled heating, at a temperature that will produce a desired vapor pressure of precursor. Preferably, the vapor pressure is one that is itself sufficient to deliver the precursor vapor to the  
10    reaction chamber 11, preferably without the use of a carrier gas. The metering system 15 maintains a flow of the precursor gas vapor from the source 13 into the reaction chamber 11 at a rate that is sufficient to maintain a commercially viable CVD process in the reaction chamber 11.

The reaction chamber 11 is a generally conventional CVD  
15    reactor and includes a vacuum chamber 20 that is bounded by a vacuum tight chamber wall 21. In the chamber 20 is situated a substrate support or susceptor 22 on which a substrate such as a semiconductor wafer 23 is supported. The chamber 20 is maintained at a vacuum appropriate for the performance of a CVD reaction that will deposit a film such as a TiN barrier  
20    layer on the semiconductor wafer substrate 23. A preferred pressure range is 0.2-5.0 Torr. The vacuum is maintained by controlled operation of a vacuum pump 24 and of inlet gas sources 25 that include the delivery system 12 and may also include reducing gas sources 26 of, for example,

hydrogen ( $H_2$ ), nitrogen ( $N_2$ ) or ammonia ( $NH_3$ ) for use in carrying out a Ti reduction reaction, and an inert gas source 27 for a gas such as argon (Ar) or helium (He). The gases from the sources 25 enter the chamber 20 through a showerhead 28 that is situated at one end of the chamber 20  
5 opposite the substrate 23, generally parallel to and facing the substrate 23.

The precursor gas source 13 includes a sealed evaporator 30 that includes a cylindrical evaporation vessel 31 having a vertically oriented axis 32. The vessel 31 is bounded by a cylindrical wall 33 formed of a high temperature tolerant and non-corrosive material such as the alloy  
10 INCONEL 600, the inside surface 34 of which is highly polished and smooth. The wall 33 has a flat circular closed bottom 35 and an open top, which is sealed by a cover 36 of the same heat tolerant and non-corrosive material as the wall 33. The outlet 14 of the source 13 is situated in the cover 36. When high temperatures are used, such as with  $TiI_4$  or  $TaBr_5$ , the  
15 cover 36 is sealed to a flange ring 37 that is integral to the top of the wall 33 by a high temperature tolerant vacuum compatible metal seal 38 such as a HELICOFLEX seal, which is formed of a C-shaped nickel tube surrounding an INCONEL coil spring. With materials requiring lower temperatures, such as  $TaCl_5$  and  $TaF_5$ , a conventional elastomeric O-ring  
20 seal 38 may be used to seal the cover.

Connected to the vessel 31 through the cover 36 is a source 39 of a carrier gas, which is preferably an inert gas such as He or Ar. The source 13 includes a mass of precursor material such as  $TiI_4$ ,

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preferably  $\text{Til}_4$ , at the bottom of the vessel 31, which is loaded into the vessel 31 at standard temperature and pressure in a solid state. The vessel 31 is filled with Til vapor by sealing the vessel 31 with the solid mass of Til therein. The Til is supplied as a precursor mass 40 that is  
5 placed at the bottom of the vessel 31, where it is heated, preferably to a liquid state as long as the resulting vapor pressure is in an acceptable range. Where the mass 40 is liquid, the vapor lies above the level of the liquid mass 40. Because wall 33 is a vertical cylinder, the surface area of Til mass 40, if a liquid, remains constant regardless of the level of depletion of  
10 the Til.

The delivery system 12 is not limited to direct delivery of a precursor 40 but can be used in the alternative for delivery of precursor 40 along with a carrier gas, which can be introduced into the vessel 31 from gas source 39. Such a gas may be hydrogen ( $\text{H}_2$ ) or an inert gas such as  
15 helium (He) or argon (Ar). Where a carrier gas is used, it may be introduced into the vessel 31 so as to distribute across the top surface of the precursor mass 40 or may be introduced into the vessel 31 so as to percolate through the mass 40 from the bottom 35 of the vessel 31 with upward diffusion in order to achieve maximum surface area exposure of the mass 40 to the  
20 carrier gas. Yet another alternative is to vaporize a liquid that is in the vessel 31. However, such alternatives add undesired particulates and do not provide the controlled delivery rate achieved by the direct delivery of the

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precursor, that is, delivery without the use of a carrier gas. Therefore, direct delivery of the precursor is preferred.

To maintain the temperature of the precursor 40 in the vessel 31, the bottom 35 of the wall 33 is maintained in thermal communication with a heater 44, which maintains the precursor 40 at a controlled temperature, preferably above its melting point, that will produce a vapor pressure of greater than about 3 Torr in the absence of a carrier gas (i.e., a direct delivery system), and a lower vapor pressure such as about 1 Torr when a carrier gas is used. The exact vapor pressure depends upon other variables such as the quantity of carrier gas, the surface area of the substrate 23, and so on. In a direct delivery system for  $TiI_4$ , particularly  $TiI_4$ , such a temperature is in the range of about 180°C to 190°C. Temperatures should not be so high as to cause premature reaction of the gases in the showerhead 28 or otherwise before contacting the wafer 23.

For purposes of example, a temperature of 180°C is assumed to be the control temperature for the heating of the bottom 35 of the vessel 31. This temperature is appropriate for producing a desired vapor pressure with a  $TiI_4$  precursor. Given this temperature at the bottom 35 of the vessel 31, to prevent condensation of the precursor vapor on the walls 33 and cover 36 of the vessel 31, the cover is maintained at a higher temperature than the heater 44 at the bottom 35 of the wall 33 of, for example, 190°C, by a separately controlled heater 45 that is in thermal contact with the outside of the cover 36. The sides of the chamber wall 33

are surrounded by an annular trapped air space 46, which is contained between the chamber wall 33 and a surrounding concentric outer aluminum wall or can 47. The can 47 is further surrounded by an annular layer of silicon foam insulation 48. This temperature maintaining arrangement

5 maintains the vapor in a volume of the chamber bounded by the cover 36, the sides of the walls 33 and the surface 42 of the precursor mass 40 in the desired example temperature range of between 180°C and 190°C and the pressure greater than about 3 Torr, preferably at greater than 5 Torr. The temperature that is appropriate to maintain the desired pressure will

10 vary with the precursor material, which is primarily contemplated as a being a titanium halide compound.

The vapor flow metering system 15 includes a delivery tube 50 of at least ½ inch in diameter, or at least 10 millimeters inside diameter, and preferably larger so as to provide no appreciable pressure drop at the

15 flow rate desired, which is at least approximately 2 to 40 standard cubic centimeters per minute (sccm). The tube 50 extends from the precursor gas source 13 to which it connects at its upstream end to the outlet 14, to the reaction chamber 11 to which it connects at its downstream end to the inlet 16. The entire length of the tube 50 from the evaporator outlet 14 to

20 the reactor inlet 16 and the showerhead 28 of the reaction chamber 20 are also preferably heated to above the evaporation temperature of the precursor material 40, for example, to 195°C.

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In the tube 50 is provided baffle plate 51 in which is centered a circular orifice 52, which preferably has a diameter of approximately 0.089 inches. The pressure drop from gauge 1 56 to gauge 2 57 is regulated by control valve 53. This pressure drop after control valve 53  
5 through orifice 52 and into reaction chamber 11 is greater than about 10 milliTorr and will be proportional to the flow rate. A shut-off valve 54 is provided in the line 50 between the outlet 14 of the evaporator 13 and the control valve 53 to close the vessel 31 of the evaporator 13.

Pressure sensors 55-58 are provided in the system 10 to  
10 provide information to a controller 60 for use in controlling the system 10, including controlling the flow rate of precursor gas from the delivery system 15 into the chamber 20 of the CVD reaction chamber 11. The pressure sensors include sensor 55 connected to the tube 50 between the outlet 14 of the evaporator 13 and the shut-off valve 54 to monitor the  
15 pressure in the evaporation vessel 31. A pressure sensor 56 is connected to the tube 50 between the control valve 53 and the baffle 51 to monitor the pressure upstream of the orifice 52, while a pressure sensor 57 is connected to the tube 50 between the baffle 51 and the reactor inlet 16 to monitor the pressure downstream of the orifice 52. A further pressure  
20 sensor 58 is connected to the chamber 20 of the reaction chamber 11 to monitor the pressure in the CVD chamber 20.

Control of the flow of precursor vapor into the CVD chamber 20 of the reaction chamber 11 is achieved by the controller 60 in

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response to the pressures sensed by the sensors 55-58, particularly the sensors 56 and 57 which determine the pressure drop across the orifice 52. When the conditions are such that the flow of precursor vapor through the orifice 52 is unchoked flow, the actual flow of precursor vapor through the tube 52 is a function of the pressures monitored by pressure sensors 56 and 57, and can be determined from the ratio of the pressure measured by sensor 56 on the upstream side of the orifice 52, to the pressure measured by sensor 57 on the downstream side of the orifice 52.

When the conditions are such that the flow of precursor vapor through the orifice 52 is choked flow, the actual flow of precursor vapor through the tube 52 is a function of only the pressure monitored by pressure sensor 57. In either case, the existence of choked or unchoked flow can be determined by the controller 60 by interpreting the process conditions. When the determination is made by the controller 60, the flow rate of precursor gas can be determined by the controller 60 through calculation.

Preferably, accurate determination of the actual flow rate of precursor gas is calculated by retrieving flow rate data from lookup or multiplier tables stored in a non-volatile memory 61 accessible by the controller 60. When the actual flow rate of the precursor vapor is determined, the desired flow rate can be maintained by a closed loop feedback control of one or more of the variable orifice control valve 53, the CVD chamber pressure through evacuation pump 24 or control of reducing



or inert gases from sources 26 and 27, or by control of the temperature and vapor pressure of the precursor gas in vessel 31 by control of heaters 44, 45.

$TiI_4$  is widely available at a purity of 99.99%. It is a purple  
5 black solid at ambient temperature (18°C-22°C) with a melting point of about 150°C, and is moisture sensitive. As shown in FIG. 1, the solid  $TiI_4$  precursor material 40 is sealed in a cylindrical corrosion resistant metal vessel 31 that maximizes the available surface area of the precursor material. Vapor from  $TiI_4$  was delivered directly, that is without the use of  
10 a carrier gas, by a high conductance delivery system into reaction chamber 11. The reaction chamber 11 was heated to a temperature of at least about 100°C to prevent condensation of deposition by-products. For precise control of the thickness of the deposited film it was desirable not to use a carrier gas.

15 The controlled direct delivery of  $TiI_4$  vapor into the reaction chamber was accomplished by heating the solid  $TiI_4$  precursor to a temperature in the range of about 180°C-190°C in order to obtain a sufficient vapor pressure greater than about 3 Torr and preferably greater than 5 Torr. This pressure was required to maintain a constant pressure  
20 drop across a defined orifice in a high conductance delivery system while delivering up to about 50 sccm  $TiI_4$  precursor to a process chamber operating in the range of about 0.1-2.0 Torr. The temperature to obtain this pressure was about 185°C with  $TiI_4$ .

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A parallel plate RF discharge was used where the driven electrode was the gas delivery showerhead and the susceptor 22 or stage for the wafer or substrate 23 was the RF ground. The  $TiI_4$  vapor was combined with a process gas containing ammonia ( $NH_3$ ) above the substrate, which had been heated to a temperature between about 300°C-500°C. Argon (Ar), nitrogen ( $N_2$ ), hydrogen ( $H_2$ ) and helium (He) could be used, either singularly or in combination, as process gases.

The deposition requirements for a TiN film from a  $TiI_4$  precursor are as follows. The deposition temperature must be less than about 650°C to protect the integrity of the underlying materials on the substrate or wafer 23. The deposition rate must be greater than about 300 Å per minute to provide an acceptable throughput. The chamber pressure can be varied to obtain a desired film thickness. For example, at a wafer temperature of about 550°C with 3000 sccm  $NH_3$  and 25 sccm  $TiI_4$  without the use of a carrier gas, a pressure of about 2.0 Torr yields a deposition rate in the range of about 500-600 Å per minute. Under these same conditions, a pressure of about 1.5 Torr yields a deposition rate of about 300 Å per minute, and a pressure of about 1.0 Torr yields a deposition rate of about 150 Å per minute. The deposited film must have low stress as measured in force per unit area. The film stress must be less than about  $1 \times 10^{10}$  dynes/cm<sup>2</sup>, and with a cracking threshold greater than about 2000 Å. The electrical resistivity of the deposited film is preferably less than about 250  $\mu\Omega$ cm. The film should exhibit 100% conformality in high aspect ratio

structures. As used herein, high aspect ratio structures have an aspect ratio greater than 8.0 and up to and including structures with an aspect ratio of 10.0 or even higher. The feature may be a via, hole, trench, etc. There should be no attack or corrosion of subsequently deposited films such as aluminum (Al) films. There must be minimal impurities, ideally less than about 2 atomic percent, in the film. Finally, the process gases such as He, Ar, H<sub>2</sub> and N<sub>2</sub> must be used in commercially reasonable quantities.

The preferred ranges for the deposition of CVD TiN films are given in Table 2, with the preferred conditions indicated in parentheses.

Slm is standard liters per minute and W/cm<sup>2</sup> is watts per centimeter squared.

Table 2

Deposition Temperature	400°C-650°C (550°C)
Deposition Rate	100-300 Å/min (300 Å/min)
Stress	1-15 x 10 <sup>9</sup> dynes/cm <sup>2</sup> (< 10 <sup>10</sup> dynes/cm <sup>2</sup> )
Film thickness with no cracking	> 4000 Å
Resistivity	85-400 μΩcm (< 200 μΩcm)
Residual Iodine	0.5-5 atomic % (< 2 atomic %)
Process Gas Required	5-40 sccm TiI <sub>4</sub> (25 sccm TiI <sub>4</sub> )

The TiN films deposited by CVD from TiI<sub>4</sub> precursors according to the invention meet all of the desired criteria; they showed no attack on a subsequently deposited Al layer and showed 100% conformality in features having aspect ratios even greater than 10.0. Higher deposition

temperatures resulted in lower resistivities, lower residual iodine concentration and higher deposition rates with no sacrifice in conformality or cracking threshold.

TiN films deposited using a  $TiI_4$  precursor according to the present invention have a higher cracking threshold than TiN films deposited using other titanium halide precursors such as  $TiCl_4$ . FIG 2 is a graph comparing the stress or cracking of  $TiI_4$  and  $TiCl_4$  based TiN films. The circles indicate a TiN film deposited at 580°C from a  $TiCl_4$  precursor. The triangles indicate a TiN film deposited at 550°C from a  $TiI_4$  precursor. The arrow indicates the point at which cracking was observed in  $TiCl_4$  films. A sharp decrease in film stress, measured in dynes/cm<sup>2</sup>, with a small increase in film thickness, measured in angstroms (Å), corresponds to widespread cracking.

As shown in FIG 2, a  $TiCl_4$  based film exhibits a rapid decrease in film stress for thicknesses less than about 1000 Å. Widespread cracking was observed on a scanning electron micrograph (SEM) of a TiN film deposited using a  $TiCl_4$  based precursor on films greater than about 600 Å. No evidence of cracking was observed at any point in  $TiI_4$  films having thicknesses greater than 4000 Å. FIG 3 is a scanning electron micrograph (SEM) of a 2000 Å crack-free  $TiI_4$  based TiN film filling a trench and deposited according to the invention. The TiN layer 60 is 2000 Å deposited on a silicon dioxide layer 62.

One reason for the higher cracking threshold for a TiN film deposited using a  $TiI_4$  precursor is the intrinsically smaller grain size in the film as compared to a TiN film deposited using a  $TiCl_4$  precursor. Films composed of a matrix of small grains would inhibit crack propagation, in comparison to films consisting of larger TiN grains. FIG. 4 is a transmission electron micrograph (TEM) of TiN films deposited by CVD according to the invention using  $TiI_4$  and  $TiCl_4$  based precursors deposited at 550°C and 580°C, respectively. As shown in FIG 4,  $TiI_4$  based films have substantially smaller grains. The smaller grains are the probable reason for the superior cracking threshold of the  $TiI_4$  based TiN films.

As shown in FIG 5 and FIG 6, the conformality of the film was dependant upon process pressure in structures having high aspect ratio features when all other process condition were identical. These conditions were as follows: a temperature of 550°C, a flow of 3 slm  $NH_3$ , and a flow of 25 sccm  $TiI_4$ . FIG 5 is an SEM of a 10:1 aspect ratio structure filled with TiN deposited by CVD at a pressure of 1.5 Torr. FIG 6 is an SEM of a 10:1 aspect ratio structure filled with TiN deposited by CVD at a pressure of 1.0 Torr.

In high aspect ratio structures, a very highly saturated process is required to form a good plug with no "keyholes". The "keyhole" effect occurs when TiN deposited in a via to form a contact plug does not completely fill the via, leaving an area termed a keyhole that does not contain TiN. This effect occurs when the via has substantially vertical

walls, that is, walls that are substantially perpendicular to the base. In a via with sloping walls, the keyhole effect is eliminated. It was observed that for filling these structures a reduced process pressure of less than about 1.5 Torr was required while maintaining gas flows of about 3 slm  $\text{NH}_3$  and 25 sccm  $\text{TiI}_4$ . Good plug fill processes are possible at lower flow rates, but only at the expense of deposition rates. Conversely, higher deposition rates are possible with flow rates higher than those stated in Table 2.

FIG 7 shows the contact resistance data for electrical test structures. A plug of Ti and TiN that was deposited according to the invention from a  $\text{TiI}_4$  precursor (closed circles) was compared to a plug filled with the typical Ti/TiN and W fill using a  $\text{TiI}_4$  precursor (open circles). The contact size was  $0.3 \mu\text{m}$  and the aspect ratio was 4:1. As shown in FIG 7, replacing the usual Ti, TiN, and W layers in filling a contact plug with Ti and TiN results in equal contact resistances. This suggested that the increase in bulk material resistivity in going from W to TiN is more than compensated by the reduction in the number of metal interfaces.

Thus the plug fill process from  $\text{TiI}_4$  is a viable solution as a replacement of the current W plug in the formation of IC devices. The contact resistance is the same using the present invention as it is with a standard W plug. This is noteworthy, considering that the bulk resistivity of TiN is fifteen to twenty times greater than for W, which has a resistivity of  $10 \mu\Omega\text{cm}$ . This emphasizes the advantage of a single process and a reduced number of interfaces in the plug.

The film deposited by the method of the invention displays characteristics important to the formation of an IC. The film has low enough electrical resistivity for low interconnect impedences, the deposition rates are sufficient for throughput considerations (greater than 100 Å/min),  
5 and the film can be deposited at a thickness greater than 0.3 μm without cracking. The method of the invention can be used to fill a feature as small as 0.15 μm in diameter and with an aspect ratio greater than 10:1.

It should be understood that the embodiments of the present invention shown and described in the specification are only preferred  
10 embodiments of the inventors who are skilled in the art and are not limiting in any way. For example, Ta films may be deposited by PECVD, TaN<sub>x</sub> films may be deposited by thermal CVD, PECVD and plasma treated thermal CVD (PTTCVD) as disclosed in, respectively, PECVD OF Ta FILMS FROM TANTALUM HALIDE PRECURSORS, THERMAL CVD OF TaN FILMS FROM  
15 TANTALUM HALIDE PRECURSORS, PECVD OF TaN FILMS FROM TANTALUM HALIDE PRECURSORS and PLASMA TREATED THERMAL CVD OF TaN FILMS FROM TANTALUM HALIDE PRECURSORS all of which are invented by Hautala and Westendorp, assigned to Tokyo Electron Limited, are copending applications filed on the same date as the present application  
20 and are expressly incorporated by reference herein in their entirety. Furthermore, Ta/TaN<sub>x</sub> bilayers may be deposited by CVD and TaN<sub>x</sub> may be used for plug fill according to the inventions as disclosed in, respectively, INTEGRATION OF CVD Ta AND TaN<sub>x</sub> FILMS FROM TANTALUM HALIDE

PRECURSORS and CVD TaN<sub>x</sub> PLUG FORMATION FROM TANTALUM  
HALIDE PRECURSORS, both of which are invented by Hautala and  
Westendorp, assigned to Tokyo Electron Limited, are copending applications  
filed on the same date as the present application and are expressly  
5 incorporated by reference herein in their entirety. Therefore, various  
changes, modifications or alterations to these embodiments may be made  
or resorted to without departing from the spirit of the invention and the  
scope of the following claims.

What is claimed is:



1. A method of filling a feature in a substrate having a titanium (Ti) film deposited therein comprising depositing titanium nitride (TiN) by providing a vapor of a Ti halide precursor to a reaction chamber containing said substrate by heating said precursor to a temperature sufficient to  
5 vaporize said precursor, then combining said vapor with a process gas containing nitrogen to deposit said TiN by a chemical vapor deposition (CVD) process.
2. The method of claim 1 wherein said feature has an aspect ratio greater than 8.0.
3. The method of claim 1 wherein said feature has a diameter less than about 0.16  $\mu\text{m}$ .
4. The method of claim 1 wherein said titanium halide precursor is titanium tetraiodide ( $\text{TiI}_4$ ).
5. The method of claim 4 wherein said substrate is heated to a temperature in the range of about 400-650°C.
6. The method of claim 4 wherein said precursor delivery is in the range of about 5-40 sccm.

7. The method of claim 4 wherein said TiN is deposited at a rate in the range of about 100-600 Å/min.
8. The method of claim 1 wherein said nitrogen containing gas is ammonia.
9. The method of claim 8 wherein said ammonia is at a flow rate of about 3 slm.
10. The method of claim 1 wherein said process is a thermal CVD process.

11. A method of providing a conformal seamless titanium nitride (TiN) plug in a high aspect ratio feature of a substrate in a reaction chamber comprising providing a pressure less than 1.5 Torr in said chamber while providing a vapor of a titanium tetraiodine precursor to said chamber at a
- 5 temperature sufficient to vaporize said precursor, then combining said vapor with a process gas containing nitrogen at a flow in the range of about 5-40 sccm to deposit said TiN by a chemical vapor deposition process.

12. A substrate comprising a high aspect ratio feature filled with a conformal seamless TiN film deposited on a Ti film from a Ti halide precursor, said TiN film capable of withstanding a stress in the range of about  $1-15 \times 10^9$  dynes/cm<sup>2</sup> and having a resistivity in the range of about 85-400  $\mu\Omega$ cm.

13. The substrate of claim 12 wherein said TiN film has a thickness of up to at least 4000 Å.

14. The substrate of claim 12 wherein said TiN film has less than about 2 atomic percent impurities.

15. The substrate of claim 12 wherein said Ti halide precursor is titanium tetraiodide.

16. The substrate of claim 12 wherein said Ti halide precursor is provided to a reaction chamber containing said substrate by heating said precursor to a temperature sufficient to vaporize said precursor, then combining said vapor with a process gas containing nitrogen, and depositing  
5 said TiN on said substrate by a chemical vapor deposition process.

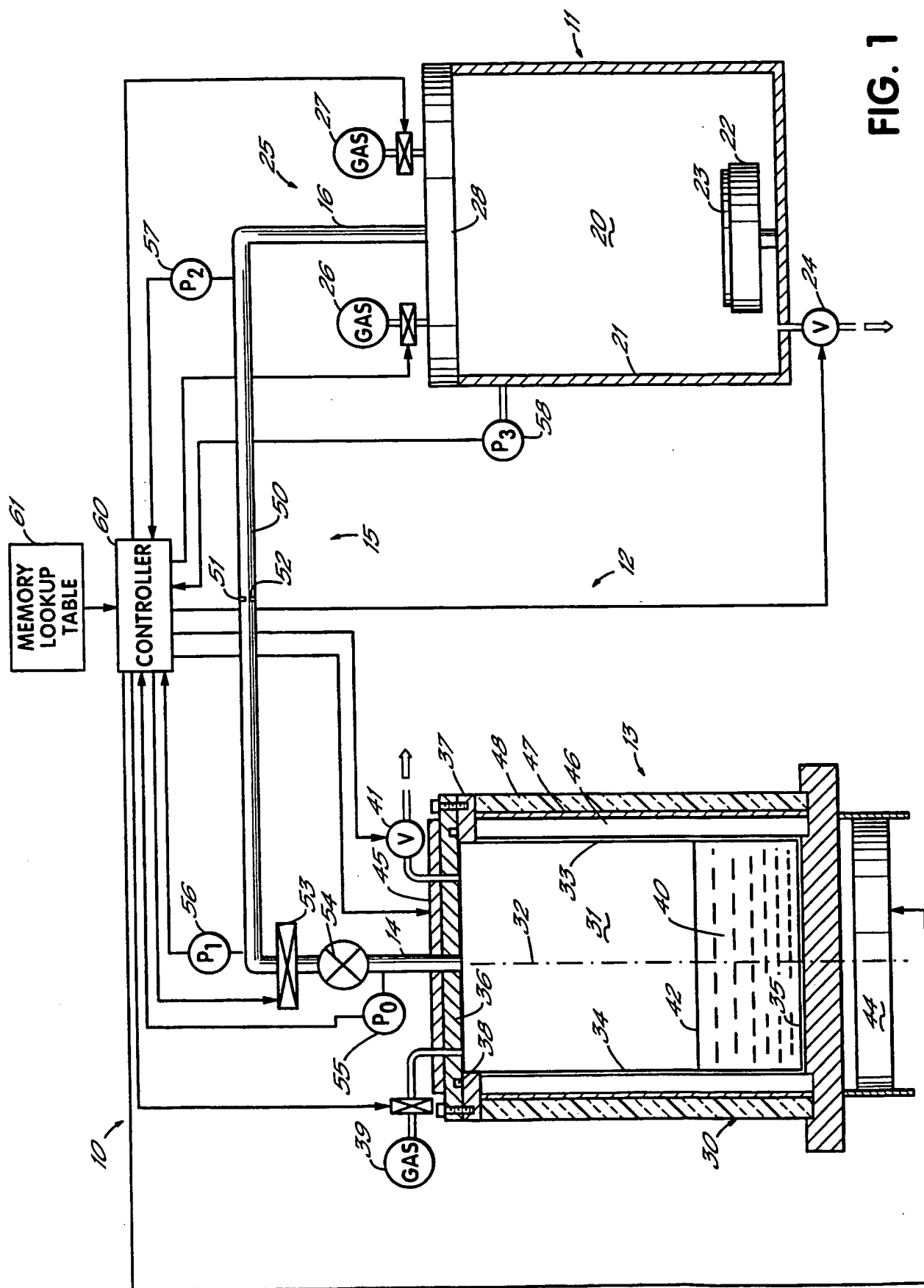


FIG. 1

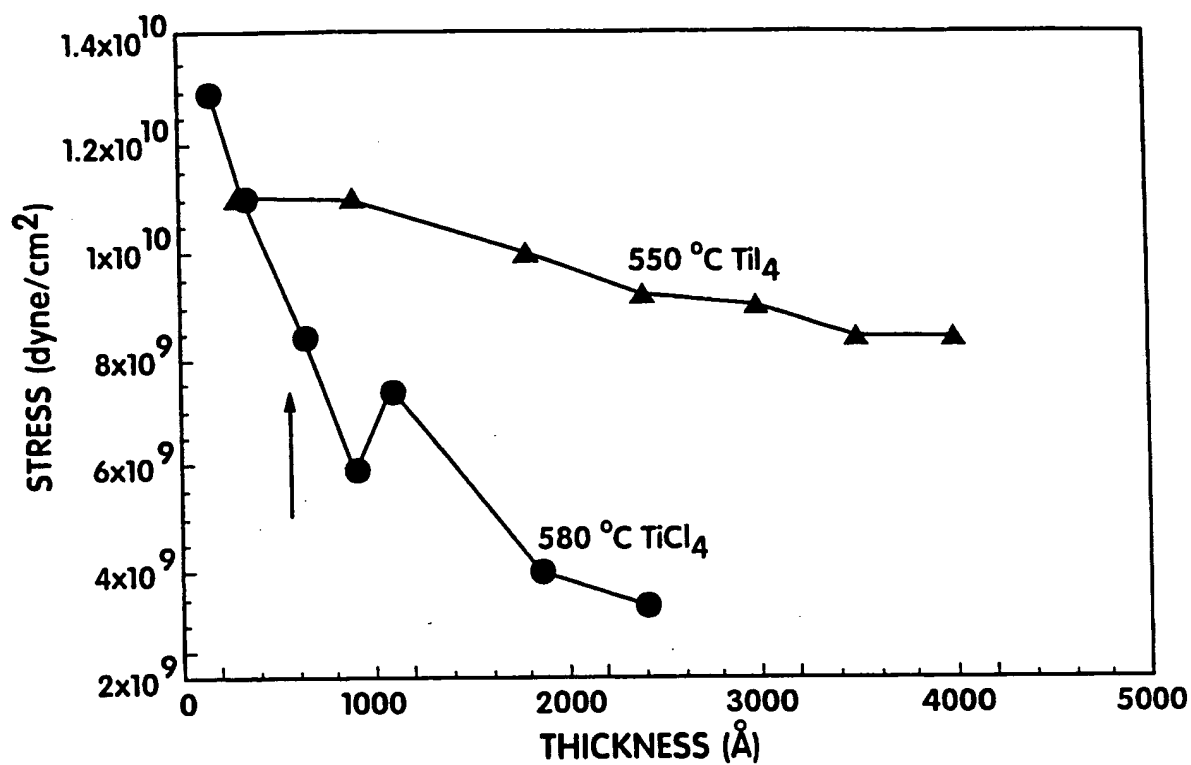


FIG. 2

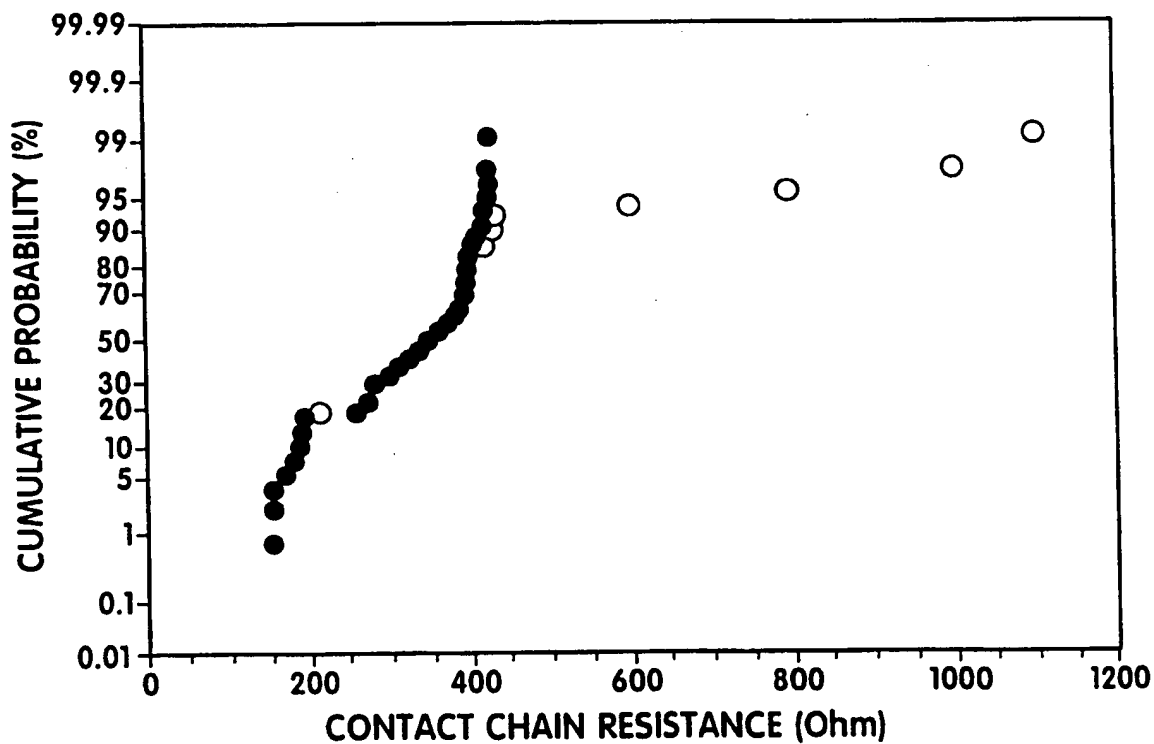
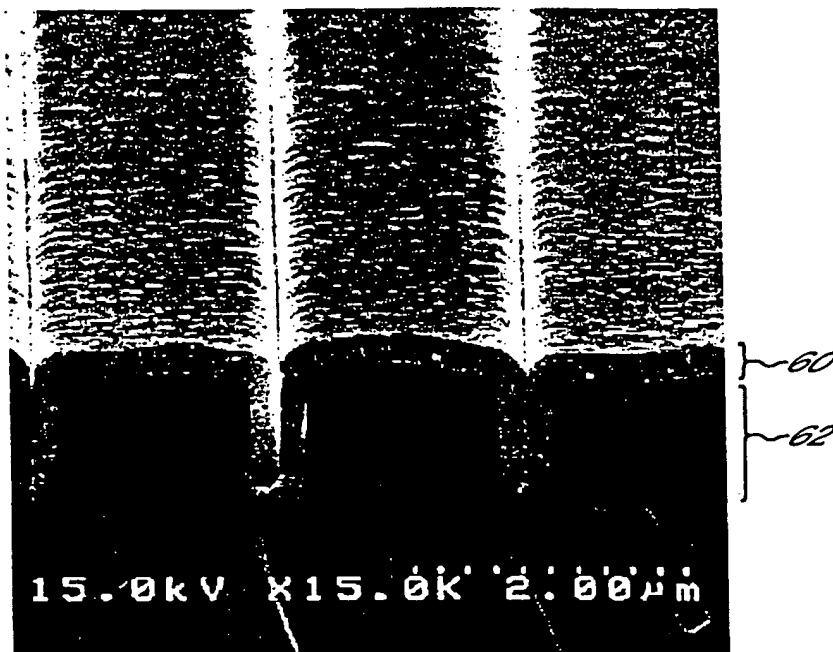
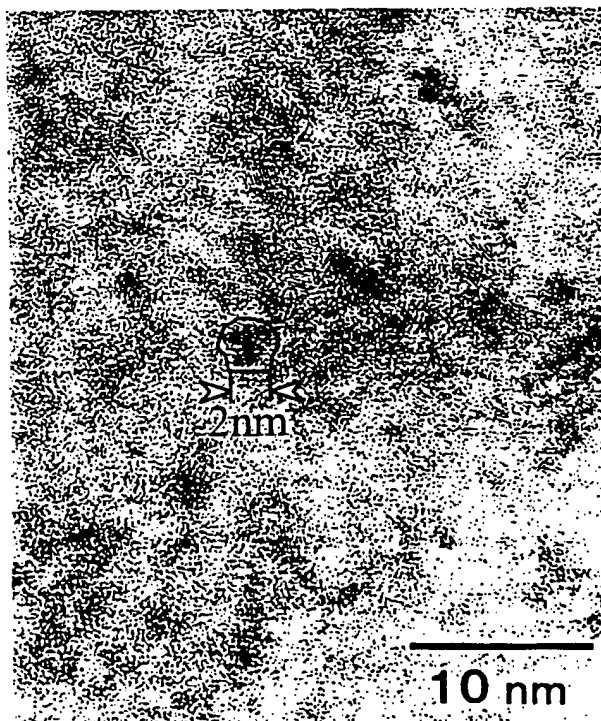
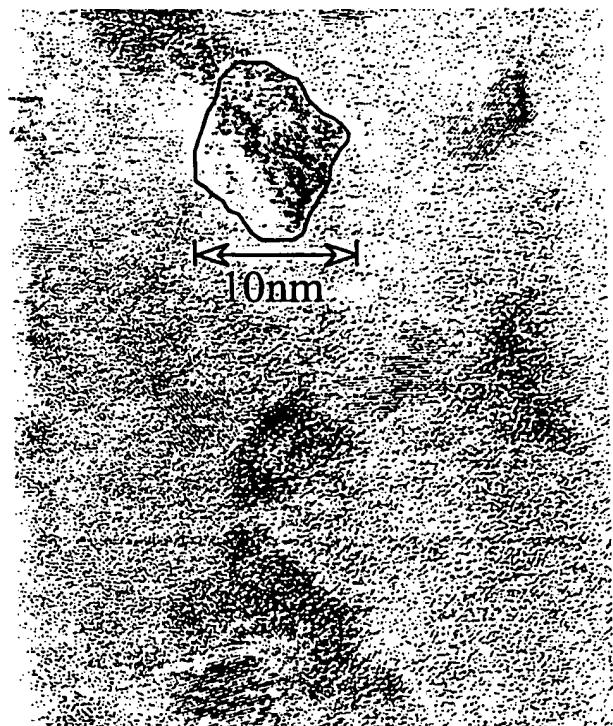


FIG. 7

**FIG. 3****FIG. 4A****FIG. 4B**

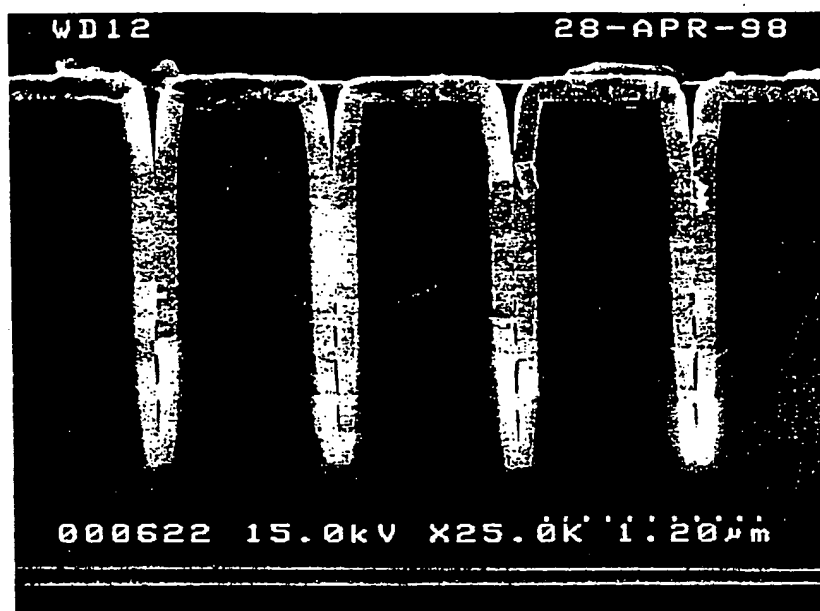


FIG. 5



FIG. 6

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## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01L21/768 H01L23/532 H01L21/285

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

INSPEC, EPO-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MEI Y J ET AL: "Characterization of TiN film grown by low-pressure-chemical-vapor-deposition" 24TH INTERNATIONAL CONFERENCE ON METALLURGICAL COATINGS AND THIN FILMS, SAN DIEGO, CA, USA, 21-25 APRIL 1997, vol. 308-309, pages 594-598, XP004110342 Thin Solid Films, 31 Oct. 1997, Elsevier, Switzerland ISSN: 0040-6090 the whole document	1,3,8,10
Y A	--- -/--	4,5,11 2,12,14

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

4 September 2000

Date of mailing of the International search report

20.09.2000

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MORI K ET AL: "Contact plug formed with chemical-vapour-deposited TiN" EXTENDED ABSTRACTS OF THE 1991 INTERNATIONAL CONFERENCE ON SOLID STATE DEVICES AND MATERIALS, YOKOHAMA, JAPAN, 27-29 AUG. 1991, pages 210-212, XP000955125 1991, Tokyo, Japan, Bus. Center Acad. Soc. Japan, Japan the whole document ---	1,8,10, 12,14
X	US 4 897 709 A (YOKOYAMA NATSUKI ET AL) 30 January 1990 (1990-01-30)	1,8,10
A	column 3, line 66 -column 4, line 64 column 7, line 10 - line 43 column 11, line 39 -column 12, line 17 column 14, line 18 - line 54; figures 1C,2,6,11,14B ---	12-14
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 09, 30 July 1999 (1999-07-30) -& JP 11 097390 A (NEC CORP), 9 April 1999 (1999-04-09)	1,8,10
A	abstract page 3, left-hand column, paragraph 3 -right-hand column, paragraph 3 page 4, right-hand column, paragraph 1 -page 5, left-hand column, paragraph 2; figures 1,2,5 ---	9,12
Y	FALTERMEIER C ET AL: "Barrier properties of titanium nitride films grown by low temperature chemical vapor deposition from titanium tetraiodide" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, MARCH 1997, ELECTROCHEM. SOC, USA, vol. 144, no. 3, pages 1002-1008, XP000938672 ISSN: 0013-4651	4,5,11
A	page 1003, left-hand column, paragraph 2 - paragraph 5 page 1005, right-hand column, paragraph 2; tables 2,4 -----	12,14

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 00/11212

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 15,16  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
Claims 15,16: The claim category is not clear, since a substrate is claimed by features of a process (Prel.Exam.Guidelines, III-4.1).
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 15,16

Claims 15,16: The claim category is not clear, since a substrate is claimed by features of a process (Prel.Exam.Guidelines, III-4.1).

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4897709 A	30-01-1990	JP 1264258 A JP 2776826 B	20-10-1989 16-07-1998
JP 11097390 A	09-04-1999	NONE	